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COATING SCIENCE AND TECHNOLOGY

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

In order to better prepare coatings for infrared laser windows, a program has been initiated to thoroughly study the science and technology of the deposition of inorganic elements and compounds as thin films. Deposition techniques include sputtering, PVD, and CVD; characterization techniques include ellipsometry, SEM, x-ray emission analysis, IR and Raman spectroscopy, ISS, AES, SIMS, and strain measurements.

Extensive theoretical calculations by Loomis have shown that effective coatings with the requisite optical properties can be prepared using two-layer

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films of the appropriate materials and thicknesses. Germanium can be utilized as the first layer on KCl, ZnSe and CdTe window materials, the second layer can be chosen (theoretically) from a number of other materials. Since this laboratory has extensive experience in the controlled deposition of germanium films, efforts are being concentrated on using this material as the first layer film.

When KCl is used as a substrate in a sputtering system, the substrate itself is sputtered away unless certain precautions are observed. A combination of low rf power, high system pressure, and large target-to-substrate distance is necessary to prevent KCl substrate sputtering and damage. The key to depositing adherent, thin films of germanium on KCl appears to be in the preparation of truly clean and scratch-free surfaces. The degree of surface perfection is being studied by ellipsometry and SEM.

Attempts to prepare tetrahedral carbon films are being made, also. Laser vaporization of graphite produces a vapor plume with well-known distributions of the various carbon species. By allowing this plume to expand into a microwave cavity, all of the carbon species are converted to C_1. These species are then deposited on the selected substrate under conditions which should lead to the preferential formation of a "diamond structure" film. PVD by laser vaporization techniques has produced only amorphous carbon films.

COATING SCIENCE AND TECHNOLOGY

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1. INTRODUCTION

The objective of this research program is to develop a thorough understanding of the science and technology of films applied as coatings on materials transparent to 10.6 and 3-5 micron radiation. The approach includes the preparation of films by sputtering, PVD and CVD techniques. Only inorganic materials are being considered; the early work is with elemental films, while more advanced work will include compounds, also. Tetrahedral carbon films are being investigated, as well. The selection of other materials will be based on crystal chemical criteria. The techniques being utilized for characterizing the films and substrates include IR and Raman spectroscopy, x-ray emission spectroscopy, scanning electron microscopy, ellipsometry, ion scattering and Auger electron spectroscopy, secondary emission mass spectrometry, and strain measurements. Both single and multilayer films will be evaluated on selected substrates. The results of these investigations will be used to provide guidelines for the selection of the best materials, processes and process controls for the production of good optical coatings for IR components at the specified wavelengths.

The requirements for good coatings must be thoroughly understood in order to plan a course of study to overcome the problems of absorption and damage to surfaces and coatings on windows used to transmit high intensity infrared laser beams. Antireflection coatings are essential, and coatings to prevent degradation by the atmosphere are often required, as well. In general coated windows must have reflectances less than 0.1%, optical absorption losses less than 10^{-4} per surface, and should be uniform to $\lambda/40$. The coatings must be moisture resistant, cleanable, adherent, and must make good thermal contact with the substrate, as well. Furthermore, the damage threshold of the coatings and surfaces must be as close as possible to the damage threshold of the bulk window materials. With these requirements in mind, one can then proceed to select coatings, with the exception of tetrahedral carbon, the two-layer systems of Loomis (1973) have been assumed to be the best solutions for those problems. Figure 1 details the first phase effort in our Laboratory.
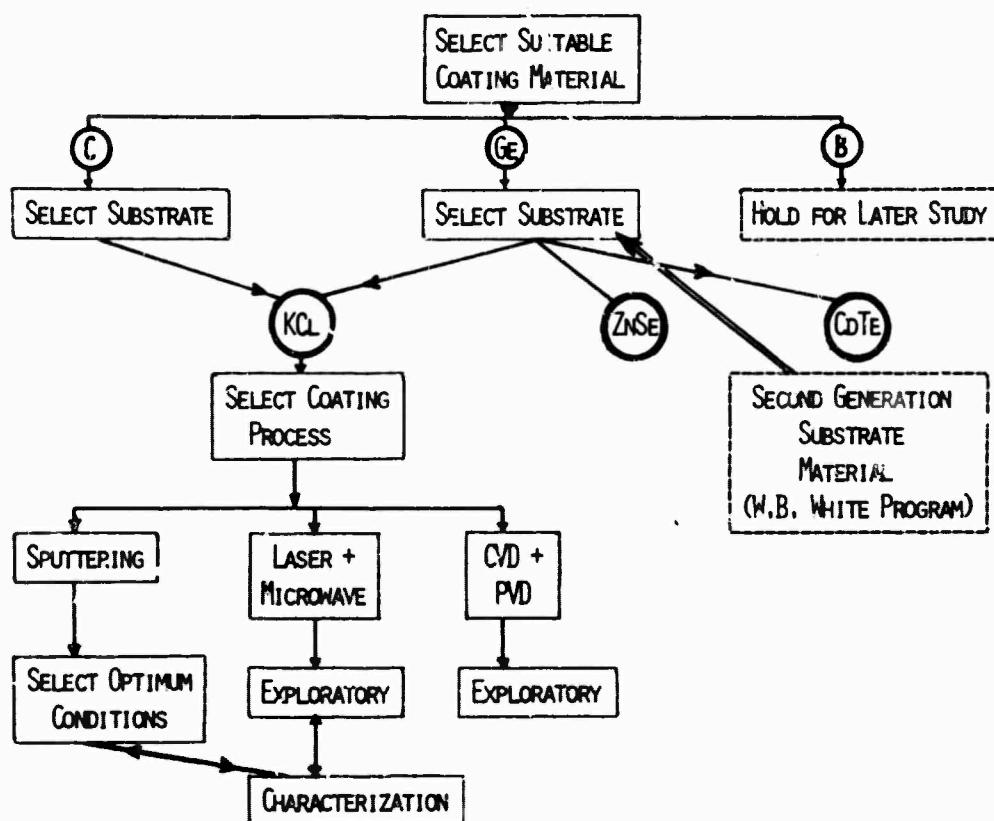
Figure 1. Flow diagram of coating-research effort at
Penn State University

2. SELECTION OF MATERIALS

2.1 Antireflection Coating - First Layer Film

According to Loomis (1973) there are a wide variety of combinations of optical films which will act as antireflection coatings on infrared transmitting substrates. One first layer film that can be used to advantage with the most reasonable choices of substrate (e.g., KCl, KCl/KBr, CdTe, ZnSe) is germanium. An extensive amount of work has been done on the preparation and characterization of non-crystalline sputtered germanium films in our Laboratory; this knowledge can be utilized in the present study and thus can result in a considerable saving of time. For instance, the macroscopic stress in a germanium film can be varied from tensile to compressive (Figure 2); the film density can be varied over a range of 25% (Figure 3); and even the argon content (inherent in the sputtering technique) can be varied from less than 0.2 to more than 5 atom percent, all as a result of
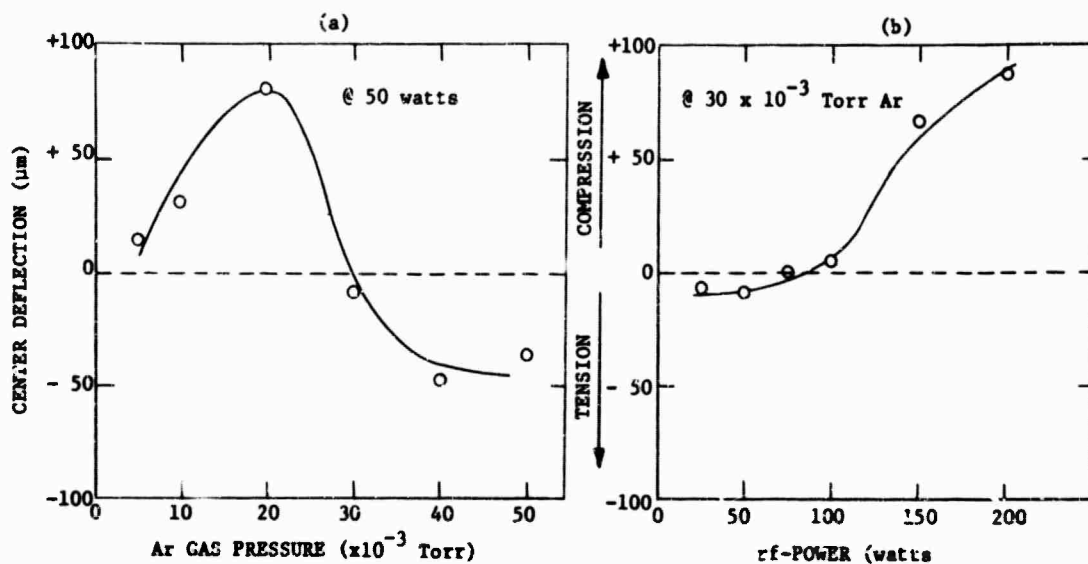
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Figure 2. Plot of macroscopic film stress as a function of (a)
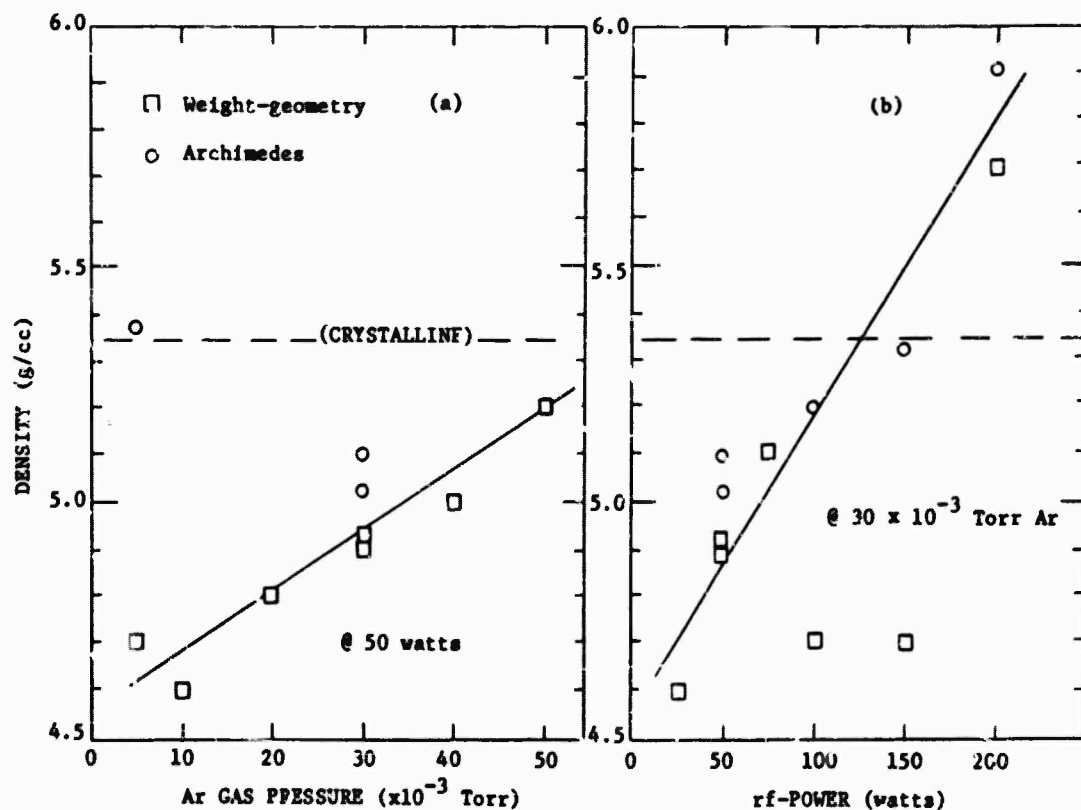argon gas pressure, and (b) rf power.

Figure 3. Plot of film density as a function of (a) argon
gas pressure, and (b) rf power.

varying just two of the sputtering parameters, rf power level and sputtering gas pressure (Messier, 1973). Thus, germanium has been selected as the first-layer film to be deposited on one or more different substrates during the initial stages of this project.

2.2 Substrate Materials

With germanium as a first layer film, several substrate materials can be used such that the specific coating characteristics mentioned earlier in this paper are satisfied. The choice was narrowed to three, KCl, ZnSe, and CdTe, based on information provided by Loomis (1973), papers presented at the Conference on High Power IR Laser Window Materials held in 1972, and prior experience with the materials, themselves. KCl was chosen as the substrate for first phase studies for a number of reasons. These included availability, cost, ease of handling and ease of polishing. Samples were cut from non-window grade single crystal material (described in detail in a later section of this paper) for the initial preparation, sputtering and adhesion tests. The next round of substrate preparation is being conducted with window-grade single crystalline material. Finally, substrates of hot-swaged, polycrystalline KCL will be used.

2.3 Second Layer Film Materials

Having chosen the first layer film and the substrate, the choice of second layer film is more restricted. Even though many materials will satisfy the optical criteria for a second layer film, one additional requirement narrows the choice considerably. Because of the nature of the sputtering process and the inability to control film thicknesses precisely, and also because film thicknesses will change due to natural environmental degradation, the effect of film thickness variation on the reflectivity of the system must be considered an important criterion in the selection of film materials. Table I, compiled from information given by Loomis (1973), shows possible second layer film materials over a first layer of germanium on three different substrates. These film materials were chosen on the basis of the insensitivity of their reflectances with relatively large variations in film thickness (±5%). In addition, our Laboratory has had reasonable amounts of experience with most of these potential second layer materials.

2.4 Summary

In summary, then, the first phase efforts of this Laboratory are being focused on using germanium as a first film coating on KCl substrate materials. Concurrently with these studies, limited efforts are being made to deposit germanium on ZnSe and CdTe. However, it is the opinion of the principal investigators and their research team that the first and most important problem to be solved at this state of the project is to be able to deposit a mechanically stable, adherent film

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on an alkali halide substrate such that theoretical transmission is achieved; hence critical efforts are focused in this direction.

Table I

Antireflection Coating Films on Different Substrates

First Layer Thickness Tolerance ± 3-5%
Absorption <0.1%

2nd Layer	
1st Layer	
Substrate	

Substrate	1st Layer	2nd Layer
KCl	Ge	ZnTe
		GaAs
ZnSe	Ge	ZnS
		CdSe
		As_2S_3
		In_2S_3
CdTe	Ge	ZnS
		ZnSe
		CdSe
		As_2S_3

(From tables compiled by Loomis, 1973)

3. SPUTTERED GERMANIUM FILMS ON KCl

3.1 Sputtering Conditions for Alkali Halides

The first problem to be solved was the sputtering away of the alkali halide substrate itself, by the high energy electrons striking its surface. This problem is peculiar to alkali halides and is caused by high energy electron generated defects called V_k centers. The defect dissociates, ejecting a halide atom, leaving the metal atom to evaporate. The result is an extremely rough surface which is incompatible with optical-grade materials. Neither the use of an rf inductor between the substrate and ground nor the use of a magnet to divert the electrons from striking the substrate proved to be effective in reducing substrate sputtering. The problem was solved using a combination of high system pressures, large target-to-substrate distances, and low sputtering power levels.

3.2 Preparation of Substrate Surfaces

Initially, the KCl substrates were prepared by cutting to size with a string saw using silicon carbide as the abrasive and glycerine as a vehicle. Because the resultant samples were so "dirty", a water polishing step was necessary. Then they were mechanically polished using 1 micron alumina with methanol, washed with ether and then chemically polished. The chemical polishing was accomplished by immersing the KCl for one minute into a stirred solution of concentrated HCl; the crystals were held by platinum-tipped forceps to prevent contamination by iron. Then they were immediately rinsed with ether and stored under ether until use. Prior to use, the ether was evaporated from the substrate with a flowing stream of dry nitrogen; the crystals were then heated with an infrared lamp to a temperature between 50° and 60°C for one hour.

To avoid contamination of the crystals during the cutting stage, they are now being cut with a nylon string saw using water as the wetting agent. With these substrates the initial water polishing step is omitted. After chemical polishing, the substrates are either used directly or subjected to reactive atmosphere processing in CCl_4. The technique has been described by Pastor and Braunstein (1973). It consists of placing the substrates in an evacuated chamber, admitting 100–120 torr of CCl_4 at room temperature, and heating to about 670°C for about 20 hours.

3.3 Characterization of Substrate Surfaces - Ellipsometry

As a result of the ASTM Conference on Laser Damage in Infrared Window Materials (1973), it is now evident that surface irregularities such as submicroscopic cracks, pits, and grooves on a scale larger than about 0.01 micrometer play the dominant role in lowering the surface damage threshold. Thus, surface characterization is essential after every operation in the preparation stage.

For such non-destructive characterization, the ellipsometric technique has been found to be quite useful and informative. As is well known, the ellipsometric parameter, Δ, is most sensitive to the thickness or the growth of non-absorbing contaminant films (Burge and Bennett, 1964; Archer, 1965), while the parameter, ψ, is dependent on the degree of perfection of the substrate itself, i.e., on the dislocation density in the surface layers of the substrate (Vedam and So, 1972) as well as on the surface roughness (Ohlidal and Lukes, 1972).

Table II lists the observed values of Δ and ψ for various samples of potassium chloride with different preparative histories. The values of Δ and ψ, calculated with the help of exact equations of ellipsometry for the ideal case of KCl substrate free of damaged surface layers as well as contaminant film, is also entered in the table.

Table II

Ellipsometric Parameters for Potassium Chloride
Substrates as a Function of Surface History

$\lambda = 5461 Å$ \qquad $n = 1.4939$ \qquad $\phi = 53°$

Surface History	ψ (deg.)	Δ (deg.)	Damaged Layer	
			n_2'	d_2' (A)
Ideal Case	2.82	0.00	-	-
Cleaved	2.89	1.07	1.492	560
Cleaved + Annealed	2.83	2.47	1.493	50
Mechanically Polished	4.99	19.51	1.440	680
Mechanically + Chemically Polished	2.90	2.45	1.489	420
Mechanically + Chemically Polished; Annealed	2.91	2.84	1.488	330

It is seen that the value of ψ (which can be determined to ±0.02°) measured
on the cleaved sample of KCl is quite different from 2.82°, the value corresponding
to the ideal case. If this difference is associated solely with the presence of a
damaged surface layer on the substrate, then the effective thickness and the
refractive index of such a damaged layer can be evaluated, and such values also are
entered in the table. It must be emphasized that no great significance should be
attached to these values, since the effect of surface roughness has been ignored
in such calculations. On annealing these cleaved samples at 670°C for 20 hours in
CCl_4 atmosphere (following the reactive atmosphere processing procedure described
by Pastor and Braunstein (1973)), it is seen the ψ_{obs} approaches that of the ideal
case, indicating that the surface is free of a damaged layer and/or surface rough-
ness. However, it is not always possible to reproduce such a sample by cleaving
procedures, since the number and distribution of cleavage steps and tear lines
with accompanying dislocations near the surface cannot be controlled.

Hence, in order to obtain specimens in a reproducible fashion, they were cut
from blanks obtained from Harshaw Chemical Company into the desired shape with the
help of a nylon string saw using water as the wetting agent. Then the specimens
were mechanically polished flat with Linde A (Al_2O_3) compound. Since the surface
layers of such a mechanically polished sample will be highly strained, it is neces-
sary to chemically polish them (in concentrated HCl at room temperature for about
1 minute) to remove the damaged layers. This is evident from the enormous decrease
in the observed value of ψ on chemically polished sample from that of the mechan-

ically polished specimen (Table II). However, the value of ψ obtained on such chemically polished specimens is still far from the ideal value. Annealing at high temperatures in CCl_4 atmosphere also did not improve the situation. Experiments with a number of other specimens with similar treatments but with varying degrees yielded almost similar results.

It may be recalled that in the case of silicon (n = 4.050, k = 0.028), almost identical values of ψ (= ψ_{ideal}) were obtained by chemical polishing treatments, even though they were carried out by different workers. Thus it appears that in the case of silicon the surface roughness does not play a dominant role in affecting the value of ψ, provided, of course, the roughness is not too coarse (Ohlidal and Lukes, 1972). The present experiments on KCl indicate that we cannot generalize from the results of silicon, that for all materials with k << n, ψ depends mainly on the damaged surface layers and not on the surface roughness. Since the KCl crystals used in the present studies were not "special window grade" specimens, it is likely that the chemical polishing may have been uneven across the face of the specimen, particularly near the small angle grain boundaries, thus creating a microrough surface. Currently, experiments are in progress with "window grade" specimens to verify the above hypothesis. Further, the samples are also being irradiated with γ-rays to radiation-harden them (Nadeau, 1963) and thus reduce the damage introduced during the mechanical polishing stage. The point defects introduced by radiation will be annealed out during the subsequent annealing stage. Once the effect of surface roughness is understood and overcome, the damaged introduced in the surface layers during deposition of the antireflecting layer can also be monitored and thus controlled.

3.4 Preparation of Sputtered Germanium Films

As mentioned before, sputtering onto KCl substrates must be done at carefully selected conditions to avoid damage to the substrate surfaces. In general, these conditions consist of a combination of low sputtering power (<50 watts), high argon pressure (<30 millitorr), and a large target-to-substrate distance (<10 cm). These conditions may change if gallium is placed under the substrate to form a more efficient heat transfer medium; this is currently under investigation. Conditions of this nature lead to germanium deposition rates of about 20Å/minute.

4. ADHESION

4.1 General

One of the major interests in this phase of the project is to learn to control the conditions which lead to optimum adherence of a film to a surface, specifically, germanium to KCl. Many different methods have been used to measure

the adhesion of films to surfaces, ranging from the "scotch tape test" to the
"Q-tip test" to the utilization of an ultracentrifuge. One method which produced
consistent and reasonable results was the "scratch test" originally used by
Heavens (1950) and analyzed by Benjamin and Weaver (1960). This technique uses a
smoothly rounded point which is drawn across the film surface. A vertical load is
applied to the stylus until the film is stripped from the surface. The applied
load is a measure of the adhesion of the film.

This method has been adopted because it is an inexpensive, quick and reliable
measure of adhesion. At the very least it will be good for comparing relative
adhesions on the same type of substrate material. Because only a small portion of
the film is removed, many tests can be performed on the same sample, and the uni-
formity of adhesion over the entire substrate area can be determined. Qualitative
comparisons between films on different substrates can also be made. Since there is
almost no literature on the adhesion of thin films, it is useful to have reliable
results to compare with our observations. Benjamin and Weaver have used this tech-
nique to study the adhesion of many different metal films to both glass (1960) and
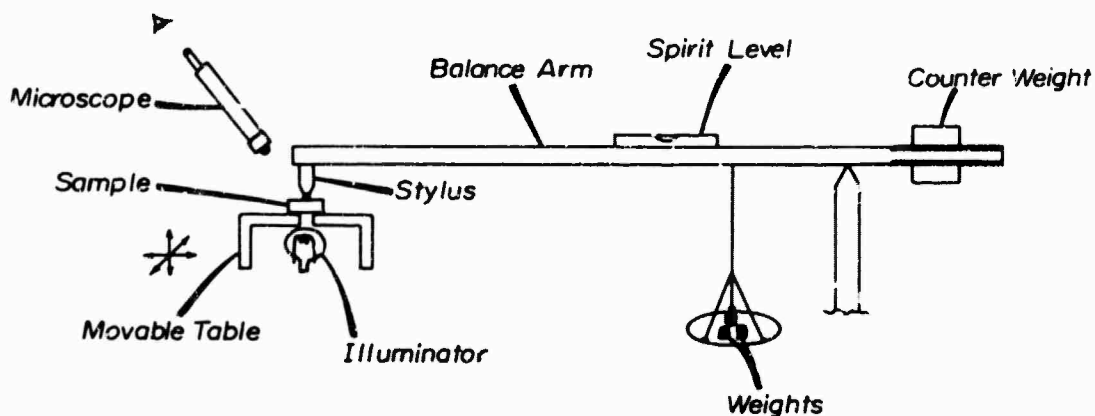alkali halide (1963) substrates.

Figure 4. Schematic drawing of scratch adhesion tester.

4.2 Scratch Adhesion Tester

Figure 4 is a schematic of the scratch tester. The instrument uses a tungs-
ten carbide dial indicator contact point (400 μm) as a stylus. This is mounted on
a balance arm which has a pan for adding weights as a load. The arm is pivoted
on hardened steel points to prevent lateral movement and facilitate rotation. The
sample is mounted on a movable stage and drawn under the stylus. The scratch is

viewed from above with a 20X microscope. The substrate is illuminated from below; thus when the critical load is applied, the film removal is easily seen as the light passes through the transparent substrate.

In addition to the "scratch test," this instrument can be converted to an abrasion tester by rotating the stage with a synchronous motor. The stylus is replaced by a tip made of "Cratex" rubber impregnated with emery.

The scratch and abrasion tests will be supplemented by other methods in the future; the tensile strength of the films will be measured and the internal stresses measured, as well.

4.3 Discussion of Germanium Film Adhesion to KCl

Benjamin and Weaver (1963) investigated the adherence of metal films to alkali halide substrates. Films of Ag, Au, Al, Cr, Cu and Cd were deposited by evaporation on the (100) faces of NaCl, KCl, and KBr. All of these films were found to adhere poorly, which was explained in terms of van der Waals bonding forces. Their calculated binding energy was 2.9 kcal/mole.

If for germanium films on KCl substrates, the bonding is also attributed to van der Waal forces similar to the examples cited above, the binding energy is calculated to be 3.8 kcal/mole. Under such circumstances, it will be necessary to create a suitable interface between the substrate and the film to produce chemical bonding and a tightly adherent film. For example, the strong adhesion of metal films to glass can be attributed to an intermediate oxide layer which produces chemically bound films. In the case of the KCl/Ge system, an attempt is being made to sputter a mixture of KCl and germanium powders onto the KCl substrate to form a graded interface between the substrate and the germanium film.

4.4 Scratch Test Measurement of Adhesion

The results of the scratch test measurements for 2 μm thick germanium films on KCl substrates with various preparative histories are shown in Table III. Clearly, there is an improvement in the adhesion when the substrates are polished. The additional improvement with the substrates washed with water prior to mechanical polishing probably results from the removal of contaminants before they can be embedded in the surface by the mechanical polishing process. The load on the glass substrates could not be increased further because of the possibility of damage to the thin glass materials which might produce unreliable results. The increased adhesion that germanium exhibits on glass probably results from an intermediate oxide layer.

The shearing force calculated for the strongest critical load case is 1.2×10^8 dynes/cm^2. Benjamin and Weaver (1963) obtained shearing forces in the range of $3.3 - 6.8 \times 10^8$ dynes/cm^2 for their metal films on KCl. Although the

Table III

Adhesion Test Results for 2 μm Thick Germanium Films

on KCl Substrates with Various Histories

Substrate History	Critical Load (grams)
KCl	
uc Polish; Cleaned with Ether after Cutting	25
KCl	
Mechanical and Chemical Polish	50
KCl	
Water + Mechanical + Chemical Polish	95
Glass Slide Cleaned with ETOH	>320

proper order of magnitude has been obtained, this is about the best correlation that can be expected from calculations of this type because of the uncertainties in the variation of adhesion with film thickness. These results support the assumption that the bonding is not of a chemical nature but due only to van der Waals forces.

5. CHEMICAL VAPOR DEPOSITION STUDIES

5.1 Background

Vapor transport methods for depositing coatings can make use of thermodynamic data in calculating the limiting rates of deposition and in determining which chemical reactions are important as a function of temperature and pressure. We utilize a special computer program for the calculation of complex chemical equilibria as functions of pressure and temperature. These calculations provide the basis for the selection of feasible chemical vapor deposition reactions and the optimum experimental conditions under which to conduct them.

5.2 CVD Deposition of Germanium

Germanium is suitable for the first coating, as has been mentioned above, and it can be deposited at "low" temperatures of about 300°C. We have constructed a flow apparatus for the preliminary studies of deposition via the germanium tetraiodide reaction scheme. Argon containing vaporized iodine is reacted with germanium metal at about 500°C to produce $GeI_2(g)$ as the principal product. The diiodide vapor flows past the substrate material which is heated to 200°-300°C, and germanium is deposited as a film. The reactions are as follows:

$$I_2(s) = I_2(g) \qquad 298°K$$

$$Ge(s) + I_2(g) = GeI_2(g) \qquad 800°K$$

$$2GeI_2(g) = GeI_4(g) + Ge(s) \qquad 500°K$$
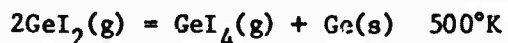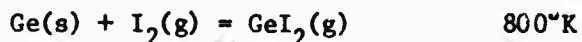
Two batches of film have been produced by this method. One film was 5.4 μm thick and had the appearance of a very rough surface. It flaked off the substrate rather easily. This film was identified as a crystalline germanium by x-ray diffraction. The other film was quite thin, but it adhered much better than the first film.

Surface of the KCl substrates become "frosted" during the CVD process. They did not become "frosted" when subjected only to a stream of argon containing $I_2(g)$. Electron microprobe analysis showed that the entire surface contained iodine, probably as the iodide replacement for the structural chloride. Only very weak chlorine signals were obtained. A probable reaction scheme for the iodine inclusion is:

$$GeI_4(g) + xKCl(s) = GeI_{4-x}Cl_x(g) + xKI(s)$$

If this is the case, one could expect the formation of all forms of GeI_{4-x}. We will attempt to discover the conditions which might make this type of reaction unfavorable. Thermodynamically, however, we might expect iodine to be even more reactive with ZnS and CdTe. Other possible reactions are also being investigated.

6. TETRAHEDRAL CARBON FILMS

6.1 Background

One of the most promising film materials for operation in the 10 micron rang is tetrahedral carbon or the so-called "diamond film." These films have been observed by mass spectrometrists for many years and appear inside their ionization chambers as a result of hydrocarbon fragmentation and pyrolysis within the spectrometer sources. Surprisingly, almost no systematic investigation of these films has ever been done, to the best of our knowledge. Many investigators have

confirmed the tetrahedral nature of these carbon films but little else has ever been done. Aisenberg and Chabot (1971) used an ion beam technique to deposit films with characteristics similar to carbon in the diamond form, but the structure was never reported. Fedosev et al. (1971) reported the fractionation of carbon isotopes in the synthesis of epitaxial films on powdered diamond substrates from methane pyrolysis. Angue, Will and Stanko (1968) also reported the growth of epitaxial diamond films on powdered diamond. Since the method of formation of these films is still a mystery, a number of techniques are being explored to grow the tetrahedral carbon films.

Our intent on outset of this project was to laser evaporate graphite and allow the plume of evaporated species (mainly C_3 and C_1) to pass through a microwave cavity in an attempt to predominately form atomic carbon which we hope might form diamond structure carbon on our substrate. We are working with the knowledge that diamond structure carbon has been found as deposits in mass spectrometer sources.

A 50 watt continuous wave CO_2 laser with ~ 6.3 mm beam diameter was used for vaporizing the graphite. Focusing was accomplished from outside the evacuated evaporation chamber using a 10" focal length antireflection coated CdTe lens. The chamber window material was sodium chloride. The flux density was in the region where the evaporation could be described as 'effusive'. Specifically, with our 10" focal length lens and 6.3 mm diameter beam of 50 watts we could theoretically get a maximum laser flux of 6.4×10^3 watts/cm^2.

Calculations show that this laser flux is too small to overcome thermal conductivity effects and, indeed, experimentally, the vaporization rate was found to be dependent on the mass of the graphite sample. The calculated minimum laser flux density required to produce vaporization with negligible thermal conductivity effects is $\sim 5 \times 10^5$ watts/cm^2. This is the region of free jet evaporation. A lens of shorter focal length could give us this density with out present setup but we would, however, have other problems with the antireflection coatings on the lens. For effective evaporization of graphite with the maximum theoretical laser flux available to use, we can use only a sample in the $1-3(mm)^3$ size range.

We have decided to discontinue the use of the CO_2 laser as a source of carbon vapor. This decision was made because we could not conveniently obtain high enough power densities to give free jet vaporization; in the effusive vaporization region there are more convenient heating arrangements that do not impose geometric restrictions and window protection problems. A carbon arc source is currently under consideration as a source of effusively vaporizing carbon vapor.

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